

CLASSIFICATION

SECRET **SECRET**CENTRAL INTELLIGENCE AGENCY
INFORMATION FROM
FOREIGN DOCUMENTS OR RADIO BROADCASTS

REPORT

50X1-HUM

CD NO.

COUNTRY USSR

DATE OF
INFORMATION 1948SUBJECT Scientific - Chemistry, esters of para-
tolylphosphonic acid.

DATE DIST. 17 Oct 1950

HOW
PUBLISHED Monthly periodicalWHERE
PUBLISHED Moscow/Leningrad

NO. OF PAGES 10

DATE
PUBLISHED Jul 1950SUPPLEMENT TO
REPORT NO.

LANGUAGE Russian

THIS DOCUMENT CONTAINS INFORMATION AFFECTING THE NATIONAL DEFENSE
OF THE UNITED STATES WITHIN THE MEANING OF ESPIONAGE ACT 50
U. S. C. 31 AND 32, AS AMENDED. ITS TRANSMISSION OR THE REVELATION
OF ITS CONTENTS IN ANY MANNER TO AN UNAUTHORIZED PERSON IS PRO-
HIBITED BY LAW. REPRODUCTION OF THIS FORM IS PROHIBITED.

THIS IS UNEVALUATED INFORMATION

SOURCE Zhurnal Obshchey Khimii, Vol XX, No 7, 1950, pp 1162-1170.

ACTION OF CARBON TETRACHLORIDE
ON ESTERS OF PARA-TOLYLPHOSPHONIC ACID

Z. L. Khisamova, Gil'm Kamay
Chem Inst imeni Acad A. Ye. Arbuzov
Kazan' Affiliate, Acad Sci USSR
Submitted 13 Nov 1948

[Tables referred to are appended.]

[This is another report describing work on phosphorus compounds being synthesized and investigated at the Kazan' Affiliate, Academy of Sciences USSR. It appears from the constitution of the compounds listed that some of them, or close analogues of them prepared in the same manner, must act as cholinesterase inhibitors, i.e., nerve poisons. Compounds of the type described may also serve as intermediates in the synthesis of substances exhibiting increased cholinesterase activity in comparison with the intermediate compound. No intention to carry out an investigation along these lines has been expressed by the Soviet investigators; this is purely conjectural and refers to a potential rather than a known or explicitly announced line of research.]

Introduction

Gil'm Kamay [1] first studied the action of CCl_4 on alkyl esters of phosphorus and phenylphosphonic acids in 1945, and showed that the esters of phosphorus acid when slightly heated, and the esters of phenylphosphonic acid even at room temperature react with CCl_4 to give esters of trichloromethylphosphonic acid and esters of phenyltrichloromethylphosphonic acid, respectively. In the course of these investigations, Kamay and his co-workers -- in that instance L. P. Yegorova -- also studied the action of CCl_4 on various alkyl esters of p-tolylphosphonic acid.

Michaelis and Páneck [2] prepared ethyl ether of p-tolylphosphonic acid with bp 240° for the first time in 1882 by reacting sodium ethylate with p-tolyl-dichlorophosphine.

CLASSIFICATION

SECRET

SECRET

STATE	<input checked="" type="checkbox"/> NAVY	<input checked="" type="checkbox"/> NSRB	DISTRIBUTION									
ARMY	<input checked="" type="checkbox"/> AIR	<input checked="" type="checkbox"/> FBI										

SECRET

SECRET

50X1-HUM

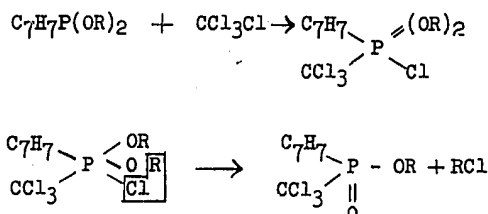
In the current paper, Kamay and his collaborator, Z. L. Khisamova, prepared alkyl esters of p-tolylphosphonic acid by the action of the corresponding alcohols with p-tolylidichlorophosphine in the presence of dimethylaniline, and data concerning these esters is given in Table 1.

These esters are readily mobile, colorless liquids with unpleasant odors; they can be distilled in vacuum without decomposing. They are hydrolyzed under the action of water to form p-tolylphosphonic acid. As derivatives of trivalent phosphorus, they react exothermically with monohalide salts of copper and alkyl halides.

The authors investigated the exothermic interaction of methyl iodide with various newly synthesized esters of p-tolylphosphonic acid.

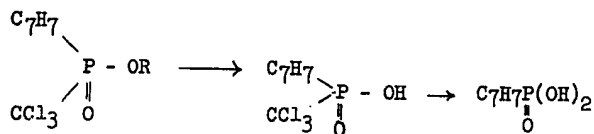
Table 2 gives data on these resulting esters of p-tolylmethylphosphinic acid, which are colorless liquids of dense consistency and weak odor. Heating them with concentrated hydrochloric acid results in their saponification to form p-tolylmethylphosphonic acid with bp 119-120°, identical to that of the compound prepared earlier by Michaelis [3].

In the present investigation, Kamay and his co-worker also studied the action of CCl_4 on esters of p-tolylphosphonic acid, and were able to show that these esters readily react exothermically and that the reaction proceeds according to the following scheme:



The esters prepared in the above manner are described in Table 3. They are colorless liquids with a characteristic pleasant odor, and can be distilled without decomposing under high pressure.

Alkyl esters of trichloromethyl-p-tolylphosphonic acid, as a result of being heated with HCl , are first saponified to form alkyl chlorides and trichloromethyl-p-tolylphosphonic acid. However, prolonged heating of the acid apparently hydrolyzes it to effect a more profound change, resulting in the formation of p-tolylphosphonic acid according to the following scheme:



The authors plan to make a more detailed investigation of the products of this hydrolysis reaction.

Experimental Section

The original product -- p-tolylidichlorophosphine -- was prepared according to the method of Michaelis and Paneck [2]. It is a colorless liquid with an unpleasant odor; b_p 120°; d_4^{20} 1.2864; d_4^{25} 1.2666; n_D^{20} 1.5886.

- 2 -

SECRET

SECRET

SECRET

SECRET

50X1-HUM

1. Preparation of Methyl Ester of p-Tolylphosphonic Acid

A total of 13.5 g of methyl alcohol, 50.2 g of dimethylaniline, and 100 ml of absolute ethyl ether were placed into a round-bottomed flask equipped with an agitator, drop funnel, and reflux condenser. Under good cooling and continuous agitation, 40 g of p-tolyldichlorophosphine were added to the mixture through the drop funnel. A large quantity of heat was liberated in the interaction. Next, the contents of the flask were boiled for 30 minutes on a water bath. The following day, the precipitated crystals of the hydrochloride of dimethylaniline were separated by filtration and then washed with dry ether. The ether was driven off from the solution on a water bath, and the residue distilled in vacuum.

b₁₄ 107-109° for the main fraction; yield: 52% of the theoretical.

0.1017 g of substance; 31.1 ml NaOH (1 ml NaOH = 0.5479 mg P)

Found % of P: 16.77

Calculated % of P: 16.85

C₉H₁₃O₂P

Methyl ester of p-tolylphosphonic acid reacted with copper monohalides.

d₀¹⁰ 1.0709; d₀¹⁰ 1.0427; n_D¹⁰ 1.5325.

2. Isomerization of Methyl Ester of p-Tolylphosphonic Acid Into Methyl Ester of p-Tolylmethylphosphinic Acid.

To a flask equipped with a reflux condenser and containing 9 g of the first compound were gradually added 5 g of methyl iodide. The reaction then proceeded, with the liberation of considerable heat, to give a yield of about 90%.

b₁₃ 151-152°

0.1315 g of substance; 40.05 ml NaOH (1 ml NaOH = 0.5479 mg P)

Found % of P: 16.67

Calculated % of P: 16.85

C₉H₁₃O₂P

d₀¹⁵ 1.1315; d₀¹⁵ 1.1204; n_D¹⁵ 1.5280

3. Saponification of Methyl Ester of p-Tolylmethylphosphinic Acid

In a flask with a reflux condenser, 5 g of the above substance and 15 ml of concentrated HCl were boiled 3 hours. After removal of the HCl, a crystalline substance was obtained, which was then recrystallized from alcohol and found to have bp 119-120°. According to Michaelis, p-tolylmethylphosphinic acid has bp 120°.

4. Preparation of Methyl Ester of Trichloromethyl-p-Tolylphosphinic Acid.

To 9.5 g of CCl₄ in a flask equipped with a reflux condenser were gradually added 12 g of the methyl ester of p-tolylphosphinic acid. The result was a violent exothermic reaction, as a result of which methyl chloride was quantitatively eliminated. The residual liquid was distilled in vacuum.

b₁ 128-130°; d₀²⁰ 1.2328; d₀²⁰ 1.2140; n_D²⁰ 1.5312

0.1238 g of substance; 23.6 ml NaOH (1 ml NaOH = 0.5459 mg P)

- 3 -

SECRET

SECRET

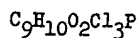
SECRET

SECRET

50X1-HUM

Found % of P: 10.41

Calculated % of P: 10.77



This compound dissolves in many organic solvents.

5. Preparation of the Ethyl Ester of p-Tolylphosphonic Acid

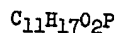
According to the method described in the introduction, from 18.1 g of absolute ethyl alcohol, 50 g of dimethylaniline, and 40 g of p-tolyl-dichlorophosphine in a medium of absolute ether was prepared the ethyl ester of p-tolylphosphonic acid.

b₉ 123-125° and yield of 19 g (or 50%) for the main fraction

0.1301 g of substance; 35.4 ml NaOH (1 ml NaOH = 0.5459 mg P)

Found % of P: 14.85

Calculated % of P: 14.63

d₄¹⁰ 1.0380; d₄¹⁸ 1.0210; n_D¹⁸ 1.5138

6. Isomerization of Ethyl Ester of p-Tolylphosphonic Acid Into Ethyl Ester of p-Tolylethylphosphonic Acid.

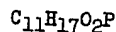
After 9 g of the first substance and 6 g of ethyl iodide were placed in a flask equipped with a reflux condenser, the contents were boiled on a water bath for 2 hours.

b₁₃ 161° for the isomerized product

0.1316 g of substance; 35.8 ml NaOH (1 ml NaOH = 0.5459 mg P)

Found % of P: 14.85

Calculated % of P: 14.63

d₄⁰ 1.0830; d₄¹⁶ 1.0697; n_D¹⁸ 1.5195

7. Preparation of the Ethyl Ester of Trichloromethyl-p-Tolylphosphonic Acid

Into a flask were put 11 g of the ethyl ester of p-tolylphosphonic acid, and 8 g of CCl₄ were then gradually added through the drop funnel to produce a marked exothermic reaction. The reaction mixture was boiled for 2 hours on a water bath, after which the liquid assumed a yellowish color.

b₂ 157° for the basic fraction

0.1265 g of substance; 0.1779 g of AgCl

0.1166 g of substance; 22.7 ml NaOH (1 ml NaOH = 0.5459 mg P)

0.1288 g of substance; 24.75 ml NaOH

Found % of P: 10.62, 10.49; of Cl: 24.79

- 4 -

SECRET

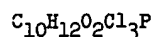
SECRET

SECRET

SECRET

50X1-HUM

Calculated % of P: 10.38; of Cl: 35.20



d_4^{20} 1.3260; d_4^{16} 1.3103; n_D^{16} 1.5428

8. Saponification of Ethyl Ester of Trichloromethyl-p-Tolylphosphinic Acid

For 2 hours, 4 g of this compound were boiled with 12 ml of concentrated HCl in a flask equipped with a reflux condenser. After removal of the HCl by multiple evaporation with water on a water bath, a crystalline substance was obtained. The crystals were soluble in alcohol and ether. After recrystallization from the latter, they were found to have the bp 184.5-185°.

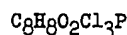
0.0922 g of substance; 19.5 ml NaOH (1 ml NaOH = 0.5459 mg P)

0.0990 g of substance; 21.1 ml NaOH

0.1056 g of substance; 0.1638 g AgCl

Found % of P: 11.54, 11.63; of Cl: 38.41

Calculated % of P: 11.35; of Cl: 38.90



9. Preparation of the p-Propyl Ester of p-Tolylphosphonic Acid

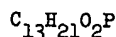
From 24 g of propyl alcohol, 50 g of dimethylaniline, and 40 g of p-tolyl dichlorophosphine in a medium of absolute ether, the above compound was prepared in the same manner as the analogous esters described previously in this article.

b_6 129-130° and yield of 81.9% for the main fraction

0.1108 g of substance; 24.8 mg NaOH (1 ml NaOH = 0.5718 mg P)

Found % of P: 12.76

Calculated % of P: 12.92



d_4^{20} 1.0091; d_4^{16} 0.9937; n_D^{16} 1.5070

10. Action of Methyl Iodide on the Propyl Ester of p-Tolylphosphonic Acid

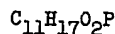
A pronounced exothermic reaction was obtained by gradually adding 8.8 g of methyl iodide through a drop funnel into a round-bottomed flask equipped with a reflux condenser and containing 15 g of the second compound. To complete the reaction, the mixture was boiled on a water bath for 3 hours.

b_{12} 167° and yield of 92% for the main fraction

0.1101 g of substance; 28.7 ml NaOH (1 ml NaOH = 0.5718 mg P)

Found % of P: 14.91

Calculated % of P: 14.62



- 5 -

SECRET

SECRET

SECRET

SECRET

50X1-HUM

The propyl ester of methyl-p-tolylphosphinic acid which is formed dissolves well in ether, chloroform, and benzene.

d_4^{20} 1.0889; d_4^{16} 1.0650; n_D^{16} 1.5185

Saponification of this substance with HCl resulted in the elimination of methyl-p-tolylphosphinic acid with bp 119-120°.

11. Preparation of the Propyl Ester of Trichloromethyl-p-Tolylphosphinic Acid

A total of 12 g of this substance were prepared from 15 g of propyl ester of p-tolylphosphonic acid and 10 g of CCl_4 .

b₃ 169-170°

0.1194 g of substance; 21.5 ml NaOH (1 ml NaOH = 0.5718 mg P)

Found % of P: 10.27

Calculated % of P: 9.84

$C_{11}H_{14}O_2Cl_3P$

This compound dissolves in organic solvents.

d_4^{20} 1.3094; d_4^{16} 1.2944; n_D^{16} 1.5370

Saponification of this ester with HCl produces trichloromethyl-p-tolylphosphinic acid with bp 184°.

12. Preparation of n-Butyl Ester of p-Tolylphosphonic Acid

A yield of 89.3% of the theoretical of this compound was obtained from 30.7 g of butyl alcohol, 50 g of dimethylaniline, and 40 g of p-tolyl-dichlorophosphine in a medium of absolute ether.

b₁₃ 170-171°

0.1168 g of substance; 24.8 ml NaOH (1 ml NaOH = 0.5519 mg P)

0.1228 g of substance; 25.4 ml NaOH

Found % of P: 11.75; 11.42

Calculated % of P: 11.57

$C_{15}H_{25}O_2P$

This ester is not soluble in water, but is readily dissolved in ether and alcohol.

d_4^{20} 0.9899; d_4^{16} 0.9776; n_D^{16} 1.5024

13. Action of Methyl Iodide on n-Butyl Ester of p-Tolylphosphonic Acid

The interaction of 5.2 g of the first compound and 10 g of the latter gave 7.6 g, i.e., about 90% of the theoretical, of n-butyl ester of p-tolylphosphinic acid.

b₁₁ 178°

d_4^{20} 1.0722; d_4^{16} 1.0583; n_D^{16} 1.5092

- 6 -

SECRET

SECRET

SECRET

SECRET

50X1-HUM

0.1124 g of substance; 27.6 ml NaOH (1 ml NaOH = 0.5519 mg P)

0.1160 g of substance 28.3 ml NaOH

Found % of P: 13.55, 13.51

Calculated % of P: 13.72

$C_{12}H_{19}O_2P$

Saponification of the butyl ester of methyl-p-tolylphosphinic acid by heating with HCl gave methy-p-tolylphosphinic acid with bp 119-120°.

14. Preparation of the Butyl Ester of Trichloromethyl-p-Tolylphosphinic Acid

Preparation of this ester is analogous to that of the methyl ester, i.e., it is accomplished by heating 10 g of the butyl ester of p-tolylphosphonic acid and 5.7 g of CCl_4 under the same conditions. After removal by distillation of the butyl chloride, the residual dense liquid was distilled in vacuum.

b_2 180-181°

d_4^{20} 1.2303; d_4^{16} 1.2143; n_D^{16} 1.5276

0.1003 g of substance; 0.1289 g AgCl.

0.1042 g of substance; 18.4 ml NaOH (1 ml NaOH = 0.5519 mg P)

0.1078 g of substance; 19.1 ml NaOH (1 ml NaOH = 0.55 k/mg)

Found % of P: 9.74, 9.77; of Cl: 32.28

Calculated % of P: 19.42; of Cl: 31.79

$C_{12}H_{16}O_2Cl_3P$

Saponification of this ester resulted in the formation of p-tolyltrichloromethylphosphinic acid with bp 184°.

15. Preparation of Isobutyl Ester of p-Tolylphosphinic Acid

From 30.7 g of isobutyl alcohol, 50 g of dimethylaniline, and 40 g of p-tolyltrichlorophosphine was synthesized the isobutyl ester of p-tolylphosphinic acid.

b_{13} 155-156° and yield of about 77%

0.1075 g of substance; 22.8 ml NaOH

0.1051 g of substance; 22.4 ml NaOH (1 ml NaOH = 0.5519 mg P)

Found % of P: 11.70, 11.76

Calculated % of P: 11.57

$C_{15}H_{25}O_2P$

d_4^{20} 0.9807; d_4^{16} 0.9667; n_D^{16} 1.4987

- 7 -

SECRET

SECRET

SECRET
SECRET

50X1-HUM

16. Preparation of the Isobutyl Ester of Trichloromethyl-p-Tolylphosphinic Acid

This substance was prepared from the exothermic reaction of 16 g of isobutyl ester of p-tolylphosphonic acid and 2.2 g of CCl_4 . Isobutyl chloride was eliminated almost quantitatively. Yield of the ester was about 58% of the theoretical.

 b_p 178-180°

 d_4^{20} 1.2661; d_4^{16} 1.2250; n_D^{16} 1.5294

0.1368 g of substance; 23.8 ml NaOH (1 ml NaOH = 0.5519 mg P)

Found % of P: 9.60

Calculated % of P: 9.42

 $\text{C}_{12}\text{H}_{16}\text{O}_2\text{Cl}_3\text{P}$

Upon heating with HCl, the product was saponified to form trichloromethyl-p-tolylphosphinic acid with bp 184°.

BIBLIOGRAPHY

1. Kamay, L. P. Yegorova, Zhurnal Obshchey Khimii (ZOK), XVI, 1521, 1946; Doklady Akademii Nauk SSSR, LV, 223, 1947 [FDD Per Abs 21T7]; Kamay, ZOK, 440, 1948.
2. Michaelis, Paneck, Lieb. Ann., CCXII, 213, 1882.
3. Michaelis, Ber., XXXI, 1046, 1898.

Table 1

No of Preparation	Substance	Bp at 6-13 mm	d_4^{20}	n_D^{16}
1	$\text{C}_7\text{H}_7\text{P}(\text{OCH}_3)_2$	107-109°	1.0709	1.5325
2	$\text{C}_7\text{H}_7\text{P}(\text{OC}_2\text{H}_5)_2$	123-125°	1.0380	1.5138
3	$\text{C}_7\text{H}_7\text{P}(\text{OC}_3\text{H}_7)_2$	129-130°	1.0091	1.5070
4	$\text{C}_7\text{H}_7\text{P}(\text{OC}_4\text{H}_9)_2$	170-171°	0.9899	1.5024
5	$\text{C}_7\text{H}_7\text{P}(\text{OC}_4\text{H}_9)_2^{\text{iso}}$	155-156°	0.9807	1.4987

- 8 -

SECRET

SECRET

SECRET

SECRET

50X1-HUM

Table 3 (Contd)

<u>No of Preparation</u>	<u>Substance</u>	<u>Bp at 2 mm Hg</u>	<u>$\frac{d_0}{0}$</u>	<u>n_D</u>
4	$\begin{array}{c} \text{C}_7\text{H}_7 \\ \diagdown \\ \text{P} - \text{OC}_4\text{H}_9 \text{ n} \\ \diagup \\ \text{CCl}_3 \\ \parallel \\ \text{O} \end{array}$	180-181°	1.2303	1.5267
5	$\begin{array}{c} \text{C}_7\text{H}_7 \\ \diagdown \\ \text{P} - \text{OC}_4\text{H}_9 \text{ iso} \\ \diagup \\ \text{CCl}_3 \\ \parallel \\ \text{O} \end{array}$	178-180°	1.2661	1.5294

- E N D -

- 10 -

SECRET

SECRET